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CHEMICAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic emulsions and more particularly to chemical sensitizers therefor.

It is well known that silver halide emulsions may be chemically sensitized with a variety of materials so as to increase the speed and generally the gamma of the emulsions as opposed to optical sensitizing in which the optical range of sensitivity is increased. Depending upon the materials and methods employed, it is generally regarded that chemical sensitization results in either the formation of silver sulfide on the surface of the silver halide crystal or results in the formation of small amounts of silver from the reduction of silver halide, which effect may be in addition to the former effect sometimes known as sulfur sensitizing. The present invention is concerned primarily with chemical sensitization apparently of the latter type.

Among the materials previously proposed for augmenting emulsion sensitivity may be mentioned basic compounds such as ammonia and certain aromatic and aliphatic amines such as triethylamine and triethanolamine; whereas other amines such as propylamylhexylamine are said to have no effect upon emulsion sensitivity. Similarly, we have found that simple polyamines such as ethylene diamine are not effective chemical sensitizers for silver halide emulsions. On the other hand, we have discovered a certain polyamine compound similar in structure to ethylene diamine which surprisingly is a powerful sensitizer for silver halide emulsions.

One object of our invention is to provide chemically sensitized silver halide emulsions of enhanced sensitivity. Another object is to provide a novel chemical sensitizing agent for photographic emulsions. Another object is to provide photographic emulsions having the sensitivity enhanced by means of both sulfur sensitizers and the novel sensitizer of our invention. A further object is to provide the methods of augmenting emulsion sensitivity utilizing the novel sensitizing agent. Another object is to provide photographic elements in which the novel emulsions are useful. Further objects of our invention will become apparent from consideration of the following description.

The objects of our invention are accomplished in part by the incorporation in silver halide emulsion layers of a polyamine compound of the structure such as spermine. Spermine has the formula

$$H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$$

and is representative of polyamines having both propylene and butylene groups separated by nitrogen atoms. In addition to the polyamine mentioned, we find equally useful for incorporation

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in emulsions the water-soluble-salts of the amine with acids having a non-desensitizing effect on emulsions such as the acetates, carbonates, sulfates and hydrochloride salts.

The novel sensitizer is incorporated in emulsions at any stage in their preparation but preferably before digestion is complete. Generally, in order to obtain the optimum sensitizing effect, we heat the emulsion after addition of the sensitizing agent. The sensitizers may be used in conjunction with other chemical and optical sensitizers such as the well known sulfur sensitizing compounds such as disclosed in Sheppard U. S. Patents 1,574,944 granted March 2, 1926, and 1,623,499 granted April 5, 1927. Our novel sensitizer may be employed before, after or simultaneously with sulfur sensitizing. Also our novel sensitizer is useful with a variety of emulsions, producing pronounced speed increases in either negative or positive types of emulsions.

Our invention will now be illustrated by reference to the following specific examples.

Example 1

100 cc. samples of a high speed bromoiodide negative type of emulsion containing silver halide from 26 grams of silver nitrate and 32 grams of gelatin were each diluted with water to 460 cc. and the pH adjusted to 6.4. To one sample of emulsion was added 0.5 mg. of spermine in aqueous solution adjusted to pH 7.0 with acetic acid. This emulsion and the control sample were heated for 45 minutes at 50° C., cooled to 40° C. and each sample further sensitized by heating at 59° C. with a sulfur sensitizing agent such as disclosed in the Sheppard patents above e. g. Allyl thiourea, until test indicated that maximum speed had been reached. After coating and drying the samples as usual, exposure in an Eastman Type Ib sensitometer (J. S. M. P. E. 17 (1931) p. 536) and developing 4 min. in the following developer, the coatings had the characteristics shown in the table following (samples A and B).

Water, about 125° F. (50° C.)	cc.	500
p-Methylaminophenol sulfate	grams	2.2
Sodium sulfite, desiccated	do	96.0
Hydroquinone	do	8.0
Sodium carbonate, desiccated	do	48.0
Potassium bromide	do	5.0

Cold water to make 1.0 liter.

Sample	Chemical sensitizer	Fog	Gamma	10/i speed
A	Sulfur type	0.13	1.5	65
B	Spermine+Sulfur	0.16	1.5	100
C	None	0.01	0.6	1.5
D	Spermine	0.01	2.8	2.1

Example 2

Two 100 cc. samples of a high speed bromoiodide emulsion, each containing silver halide obtained from 20 grams of silver nitrate and peptized with a gelatin derivative by the process of the Lowe et al. U. S. application Serial No. 768,478, filed August 13, 1947, were adjusted to pH 6.0. To one sample was added 4 mg. of spermine in aqueous solution adjusted to pH 6.0, and both samples were then heated for 30 minutes at 50° C. After coating and drying the samples as usual, exposure was made on the Ib sensitometer and development carried out in the following developer.

Water	liters	1
p-Methylaminophenol sulfate	grams	0.3
Hydroquinone	do	6.0
Sodium sulfite (dry)	do	38.0
Sodium bisulfite	do	1.2
Sodium carbonate (dry)	do	19.0
Potassium bromide	do	0.9
Citric acid	do	0.7

The exposed and processed samples were found to have the characteristics shown in the above table (samples C and D).

It will be apparent from consideration of the above data that spermine is effective in producing large speed increases in emulsions treated therewith, in most cases the increases with sulfur sensitized emulsions being considerably greater than expected from the activity of the individual sensitizers when used alone. However, the speed increases obtained in absence of sulfur sensitizing are appreciable and valuable.

In the manner of the above examples, other types of silver halide emulsions may be treated with our novel sensitizing agent alone or in conjunction with other chemical or optical sensitizers. The amount of sensitizing agent may, depending upon the type of emulsion used, vary somewhat from the optimum amounts employed in the above examples, one-fifth to five times as much sensitizing agent producing emulsions of useful sensitivity. As is apparent, less heating is usually required when the larger amounts are employed and conversely when using the smaller quantities of sensitizing agent.

It will be noted in the above examples that the sensitizing of the emulsions with the novel compound was effected at relatively low pH. This is not a limitation of our invention but more an advantage thereof since we are able to suppress sulfur sensitivity by lowering the pH of the emulsion and since the novel sensitizer is so active, further sensitization takes place even substantially below the neutral point when it is added to the emulsion.

The novel sensitizers may, in general, be employed in hydrophilic colloid emulsion vehicles; for example, gelatin, polyvinyl alcohol, partially hydrolyzed cellulose esters, such as cellulose acetate and co-polymers of polyvinyl alcohol. The ratio of colloid to silver halide present during the digestion is not critical in this type of sensitizing since the digestion conditions can be readily adjusted as is well known in the art of sulfur sensitizing. The sensitizers are suitable for the well known types of silver chloride, silver bromide and silver iodide emulsions and emulsions containing mixtures of these halides, containing the usual emulsion addenda such as antifoggants, spreading agents, coupler compounds, etc. Such emulsions are suitable to use in forming single as well as multilayer film useful in color photography which customarily include two or more emulsion layers on a support sensitized to different regions of the visible spectrum and may or may not contain coupler compounds. According to our invention such color films carry at least one emulsion layer containing a sensitizing agent of our invention.

Our invention having been described, we would have it understood that the preceding description is by way of example only and that our invention is to be taken as limited only by the scope of the appended claims.

What we claim is:

1. A light-sensitive photographic emulsion comprising silver halide and a polyamine sensitizing agent selected from the group consisting of spermine and its water-soluble salts of non-desensitizing acids.

2. A light-sensitive photographic emulsion comprising silver halide and spermine as a sensitizing agent.

3. A light-sensitive photographic emulsion comprising sulfur sensitized silver halide and as an additional sensitizing agent a sensitizing agent selected from the group consisting of spermine and its water-soluble salts of non-desensitizing acids.

4. A light-sensitive photographic emulsion comprising sulfur sensitized silver halide and spermine as an additional sensitizing agent.

5. The method of increasing the speed of a photographic silver halide emulsion which comprises imparting sulfur sensitivity to said emulsion and effecting a further increase in sensitivity by treatment of said emulsion with a sensitizing agent selected from the group consisting of spermine and its water-soluble salts of non-desensitizing acids.

6. The method of increasing the speed of a photographic silver halide emulsion which comprises imparting sulfur sensitivity to said emulsion and effecting a further increase in sensitivity by treatment of said emulsion with spermine.

7. The method of sensitizing a photographic silver halide emulsion which comprises digesting said emulsion in the presence of a sulfur sensitizing agent and a sensitizing agent selected from the group consisting of spermine and its water-soluble salts of non-desensitizing acids.

8. The method of sensitizing a photographic silver halide emulsion which comprises digesting said emulsion in the presence of a sulfur sensitizing agent and spermine.

9. The method of sensitizing a photographic silver halide emulsion which comprises imparting sulfur sensitizing to said emulsion, adjusting the pH of said emulsion to below neutrality and further sensitizing said emulsion by digestion of said emulsion in the presence of spermine and its water-soluble salts of non-desensitizing acids.

10. The method of sensitizing a photographic silver halide emulsion which comprises imparting sulfur sensitizing to said emulsion, adjusting the pH of said emulsion to below neutrality and further sensitizing said emulsion by digestion of said emulsion in the presence of spermine.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Country	Date
496,049	Great Britain	Nov. 21, 1938